MICROCOPY RESOLUTION TEST CHART

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1. REPORT NUMBER TR-1	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Separating Polymer Solutions Using High pressure LCST Phenomena	5. TYPE OF REPORT & PERIOD COVERED Technical Report, Interim July 1, 1983 - June 30, 1984 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Alan K. McClellan and Mark A. McHugh	8. CONTRACT OR GRANT NUMBER(s) N00014-83-K-0613
9. PERFORMING ORGANIZATION NAME AND ADDRESS Mark A. McHugh Department of Chemical Engineering Univ. of Notre Dame, Notre Dame, IN 46556	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR625-841
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, 612A:BAR Department of the Navy, 800 N. Quincy Street Arlington, Va. 22217	12. REPORT DATE 10/30/84 13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) (same)	15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale;
its distribution is unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

To be published in The Journal of Polymer Engineering and Science

18. SUPPLEMENTARY NOTES

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ELECTE
MAR 18 1985
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Thermodynamic, Polymers, lower critical solution temperature, supercritical fluid.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See the next page

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Experimental results for the poly(ethylene-co-propylene) - hexane - SCF ethylene system are shown as an example of the type of phase behavior observed with polymer - solvent - SCF additive solutions. Adding 20% (w/w) ethylene to the polymer solution lowers the temperature of the LCST by 109°C. The addition of 30% (w/w) ethylene to the polymer solution lowers the temperature of the LCST curve sufficiently to merge this curve with the UCST curve.

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OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0613

Task No. NR 625-841

Technical Report No.1

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by

Alan K. McClellan and Mark A. McHugh

Prepared for Publication

in the

Journal of Polymer Engineering and Science

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	

By
Distribution/
Availability Codes

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November 9, 1984

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October 1984

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Introduction

One common method for recovering polymer from solution is to steam strip the solvent from the solution. This separation technique can lead to thermal degradation of the polymer, due to the high temperatures involved in this process. Alternatively, polymer can be recovered from solution by heating the polymer solution until it splits into two phases, a solvent rich phase, and a polymer rich phase. This phase split occurs at the lower critical solution temperature (LCST). LCST behavior of polymer solutions, has been known since the early 1960's (1), and has been found to exist for all polymer solutions unless the polymer thermally degrades before the necessary temperature is reached (2).

In the early 1970's a number of patents were filed which suggested that phase splitting at the LCST is a more efficient technique for separating polymer solutions than steam stripping. Caywood (3) shows how to separate a solution of poly (ethylene-co-propylene) in hexane at the LCST. However, due to the high temperatures involved, it is necessary to add stabilizers to the polymer solution to minimize the thermal degradation of the polymer. Anolick et al. (4,5) also demonstrate that

ethylene copolymers can be separated from their solvents (generally hexane) at the LCST. Although high temperatures are needed to induce the polymer-solvent phase split, Anolick et al. claim that better separations are obtained using this type of separation technique rather than steam stripping. However, the main limitation to separating polymer solutions at the LCST is that the solution must be heated to temperatures which are close to the critical temperature of the solvent which for good polymer solvents can be quite high (e.g., the critical temperature of cyclohexane is 287.2^0C).

Irani et al. (6) address the problem of shifting the LCST to lower temperatures by introducing a light supercritical fluid (SCF) additive to the polymer solution. The SCF additive has the effect of lowering the critical point of the solvent (now a mixed solvent) and, hence, LCST separations are obtained at much lower temperatures. Using this technique the possibility of polymer degradation is minimized and the thermal energy requirements for the process are lowered.The objective of our work in this area is to expand the data base on polymer - solvent - SCF additive mixtures. In this paper we show how the knowledge of the phase diagrams of simple binary mixtures can be used to interpret and extend the

experimentally observed phase behavior of multicomponent polymer -

solvent systems.

Phase Diagrams For Polymer-Solvent Systems

Since most polymers are polydisperse, polymer - solvent mixtures

are, in fact, multicomponent mixtures. It is also common practice to use

multicomponent solvents in the polymer process industry. Although the

phase behavior of multicomponent mixtures can be quite complex, it is

possible to use the pressure-temperature (P-T) diagrams for the limiting

case of a simple binary mixture to describe the phase behavior of polymer

solutions (7).

Using the Van der Waals equation of state Scott and van Konynenberg

(8,9) demonstrate that virtually all of the experimentally known binary

phase behavior can be schematically represented by five types of P - T

diagrams. Shown in Figure 1 are three of the diagrams which are pertinent

for this discussion. Figure 1a depicts the phase behavior for a binary

mixture where the two pure component vapor liquid equilibrium lines end

in the pure component critical points, C1 and C2. The dashed line is the

critical mixture curve running continuously from C1 to C2. Since the

liquids are not miscible at all temperatures, a liquid - liquid - vapor (LLV) line ending in an upper critcal end point (UCEP) exists at temperatures lower than the critical temperature of either component. The upper critical solution temperature (UCST) line, beginning at the UCEP, represents the effect of pressure on the transition from two liquid phases to one liquid phase.

Figure 1b represents a slightly more complicated phase diagram. Here the critical mixture curve is not continuous, but intersects the liquid immiscibility region near the critical temperature of the lighter component. The critical mixture curve which starts at C2 ends at the LCST and the branch of the critical mixture curve starting at C1 ends at the UCEP. At lower temperatures the region of liquid immiscibility again exists as shown in Figure 1a. This type of phase behavior has been found for binary polymer - solvent systems (2,10 - 14).

Shown in Figure 1c is the P-T projection of the phase diagram for a mixture in which the components differ in size, shape, and/or polarity. Here the three phase LLV line is only intersected once by the critical mixture curve at the UCEP. The other branch of the critical mixture curve, which starts at C2, never meets the LLV line or the critcal point of the

lighter component.

Shown in Figure 2a is a schematic P-T diagram for a polymer - solvent mixture. The phase behavior depicted in this diagram is very similar to that shown in Figure 1b except now the LLV line is indistinguishable from the vapor pressure curve of the solvent. In this figure the critical mixture curve is now termed the LCST curve since the phase transitions which occur along the critical mixture curve are more representitive of liquid + liquid→liquid transitions as compared to liquid + gas→fluid transitions. The intersection of the LCST curve with the solution vapor pressure curve is termed the lower critical end point (LCEP) (12).

Shown in Figure 2b is a schematic representation of the phase behavior observed by Irani et al. (6), when a light SCF additive is introduced into the mixture. The phase border curves for the solution with an SCF additive are shifted to much lower temperatures, although they are not altered in shape. Therefore, the liquid - liquid phase split of the polymer solution occurs at moderate temperatures.

The phase border curves for the poly(ethylene-co-propylene) - hexane - supercritical fluid (SCF) additive and polystyrene - toluene - SCF additive systems are described in this paper. The experimental techniques

used for obtaining high pressure phase behavior information as well as the

modelling of the phase behavior are briefly described in the following

sections.

Experimental

The experimental apparatus and procedure used in this study are

described in detail elsewhere (7), and therefore, will only be briefly

described here.

A measured amount of polymer solution is first loaded into a high

pressure, variable volume equilibrium cell. The concentration of the

polymer in the organic solvent is normally maintained at approximately 5%

(w/w) to ensure that the cloud point curves that are obtained are very

close to the actual LCST curve (12,15). A known amount of the SCF

additive is then added to the equilibrium cell.

The high pressure, variable volume equilibrium cell is designed to

operate to 35 MPa and 260°C. The cell contents, illuminated by a fiber

light pipe, are viewed through a quartz window, which is secured by a cell

end-cap. The contents of the cell are mixed by a stirring bar, activated by

a magnet, which is located below the cell. The volume of the cell is varied

by a movable piston, hence, the phase boundaries are visually obtained at a

fixed overall composition.

Phase Behavior of Polymer-Solvent-SCF Additive Mixtures

The phase behavior of the poly(ethylene - co - propylene) (EP) - hexane - ethylene system is described to highlight the characteristics of the phase behavior which can be exhibited by polymer - solvent - SCF additive mixtures. The EP used in these studies is a random copolymer of 53.8 mole% propylene, with a M_w =145,000 and M_n =67,000. The hexane solvent is a mixture of isomeric hexanes (2.5 % (w/w) 3-methyl pentane, 9.5 % (w/w) methyl cyclopentane, 88.0 % (w/w) n-hexane).

Shown in Figure 3 are the phase border curves of the EP - hexane - ethylene system with loadings of 9.9, 13.8, and 20.0 % (w/w) ethylene. (These loadings of ethylene are based on overall weight fractions). The LCEP for the EP - hexane mixture without ethylene is 174^0C. Therefore, by adding 9.9% ethylene the LCEP is decreased to 108^0C while adding 20% ethylene decreases the LCEP to 65^0C, a shift in the LCEP of 109^0C.

In an effort to further reduce the LCEP, still higher loadings of ethylene are added to the polymer solution. However, for a concentration of ethylene of 30 % (w/w) the shape of the LCST curve is radically changed, as shown in Figure 4. The LCST curve, which now does not intersect the LLV line, has merged with the UCST line. Hence, the phase behavior has changed from that depicted in Figure 1b to that shown in Figure 1c. The effect of the SCF additive is to shift the UCST curve to higher temperatures while simultaneously shifting the LCST curve to lower temperatures, until both curves merge into a single curve.

The merging of the LCST and the UCST curves with increasing concentration of the SCF additive is not unique to ethylene. This behavior has in fact, been shown to occur when methane is used as the SCF additive (7).

Further experimental studies are in progress with various polystyrene – toluene – SCF additive mixtures. This system exhibits many of the same phase behavior characteristics of the EP – hexane – ethylene system although in this instance the polystyrene is fairly monodisperse (M_n = 124,700 , M_w = 118,000), and the polymer solvent, toluene, is pure.

The SCF additive acts as a non-solvent in these systems. However, the degree of non-solvent behavior can be controlled by varying the hydrostatic pressure of the system. As shown by Patterson (16), pressure has a dramatic effect on the LCST curve. When the pressure is isothermally increased, the free volume of the solvent decreases at a much faster rate than that of the polymer. At a high enough pressure the difference between the free volume of the polymer and the free volume of the solvent decreases sufficiently to allow these components to become totally miscible.

Modelling

As a first approximation the shift in the temperature of the LCEP can be related to the critical temperature of the solvent. Figure 5 shows the temperature of the LCEP plotted against the critical temperature of the solvent. The critical temperature of the mixed solvents used for the EP – hexane – SCF additive mixtures is determined using Kay's mixing rule:

$$T_{c,mixture} = \sum_{i=1}^{n} x_i T_{ci}$$

where x_i represents the mole fraction of component i in the solvent

mixture on a polymer free basis, and T_{ci} represents the pure component

critical temperature.

Also plotted in Figure 5 is the LCEP data of Charlet and Delmas (17)

for EP – solvent mixtures where the EP polymer has the same propylene

content as the EP polymer used in our studies. For most cases the data are

well represented by a single curve. It is interesting that even the data for

a non-hydrocarbon SCF additive, carbon dioxide, are well represented by

this single curve, since Kay's mixing rule does not account for differences

in the chemical nature of the components.

This simple correlation method has a number of limitations. It does

not give any indication of the pressure at the LCEP. It also does not

indicate the concentration of the SCF additive needed to merge the LCST

and UCST curves.

Patterson's theory of corresponding states is an alternative method

to the simple correlation for predicting the location of the LCST curve and

the concentration of SCF additive needed to merge the LCST and the UCST

curves. Although Patterson's theory predicts the correct shapes of the

LCST and UCST curves their location can be shifted by as much as 100

degrees from the experimentally determined curves (18). The discrepancy

between theory and experiment is probably due to the pure component

reduction parameters used in the model. These reduction parameters are

assumed to be independent of temperature and pressure. Since wide ranges

in temperature and pressure are being used in this study, further efforts

at modelling the phase behavior will incorporate temperature and pressure dependent pure component parameters. Patterson's theory also neglects the polydispersity of the polymer, which, as described by Koningsveld (19) can have a dramatic effect on the phase behavior of the solution. It is also possible to account for polydispersity by modifying the original free volume theory. With these modifications to the free volume theory, we expect the model to be suitable for engineering calculations.

Conclusion

Separating polymer solutions using LCST phenomena is a viable alternative to steam stripping. By adding an SCF additive to the polymer solution it is possible to shift the LCST curve to lower temperatures and thus decrease the thermal energy costs of the process and reduce the possibility of thermally degrading the polymer.

In this work we have shown that the phase behavior of polymer solutions can be interpreted in terms of the phase diagrams of simple binary mixtures. These phase diagrams, which are classified by Scott and van Konynenburg, offer a useful tool for understanding the phase behavior which can be exhibited by polydisperse polymer – solvent mixtures.

The shift of the LCST curve with the addition of an SCF additive can be correlated to the critical temperature of the mixture. Patterson's theory can be used to predict the location of the LCST curve if temperature and pressure dependent pure component parameters are used and if the polydispersity of the polymer is accounted for explicitly.

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Figure 1   Schematic P-T diagrams for binary mixtures (8,9).

Figure 2   (a) Representative P-T diagram for polymer-solvent
              mixtures. (b) Schematic representation of the effect of
              an SCF additive on the phase boundary curves of a
              polymer-solvent mixture. (i) P-T projection of the phase
              boundary curves for a polymer-solvent mixture without an
   SCF additive added to the mixture, (ii) same as (i) but with
              the SCF additive.

Figure 3   Effect of ethylene on the phase border curves of the
              poly(ethylene-co-propylene) - hexane system.

Figure 4   Phase behavior of the poly(ethylene-co-propylene) - hexane
              - ethylene system.

Figure 5   Effect of the solvent critical temperature on the LCEP
              temperature. The shaded circles represent the data
              obtained by McHugh and Guckes (7) for
              poly(ethylene-co-propylene) - hexane - SCF additive
              mixtures, while the open circles represent the data
              obtained by Charlet and Delmas (17) for
              poly(ethylene-co-propylene) - solvent mixtures.
                 1. 10.8% (w/w) methane system
                 2. 20.0% (w/w) ethylene system
                 3. 13.8% (w/w) ethylene system
                 4. 13.5% (w/w) carbon dioxide system
                 5. 2 methyl butane
                 6. 9.9% (w/w) ethylene system
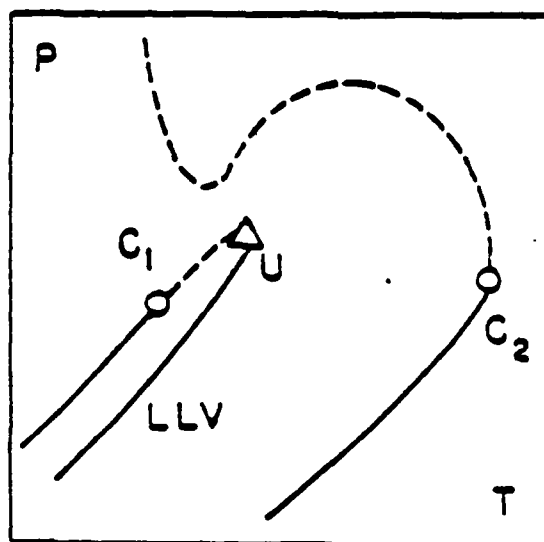
7. n-pentane

8. 2,2 dimethyl butane

9. 13.1% (w/w) propylene system

10. 8.0% (w/w) propylene system

11. 2,3 dimethyl butane

12. n-hexane

13. 2,4 dimethyl pentane

14. 2,2 dimethyl pentane

15. 2,2,3 trimethyl pentane

16. 2,3 dimethyl pentane

17. 2,2,4 trimethyl pentane

18. n-heptane

19. 3-ethyl pentane

20. n-octane

21. cyclohexane

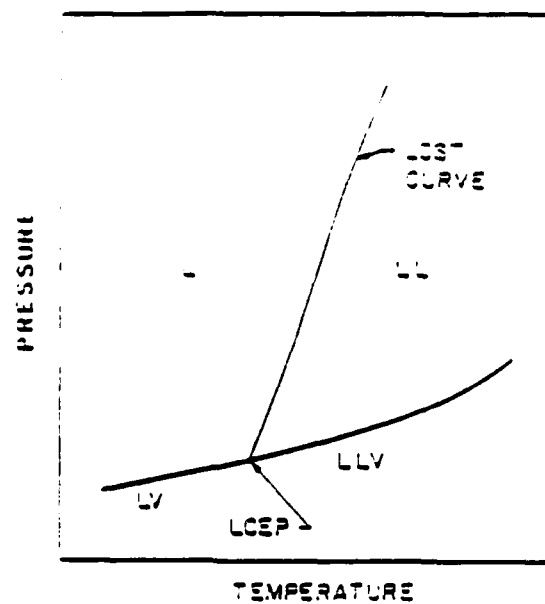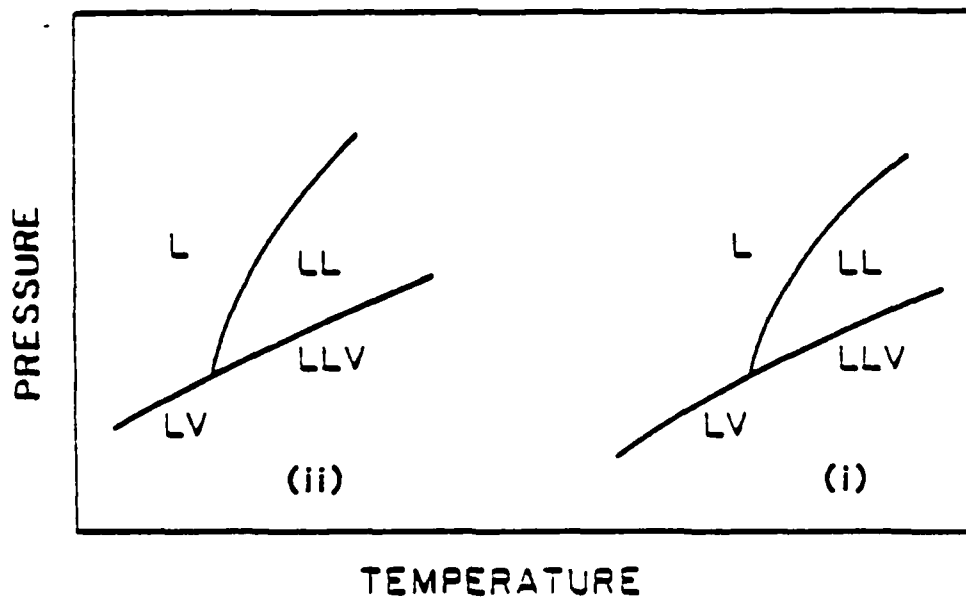22. 2,3,4 trimethyl hexane

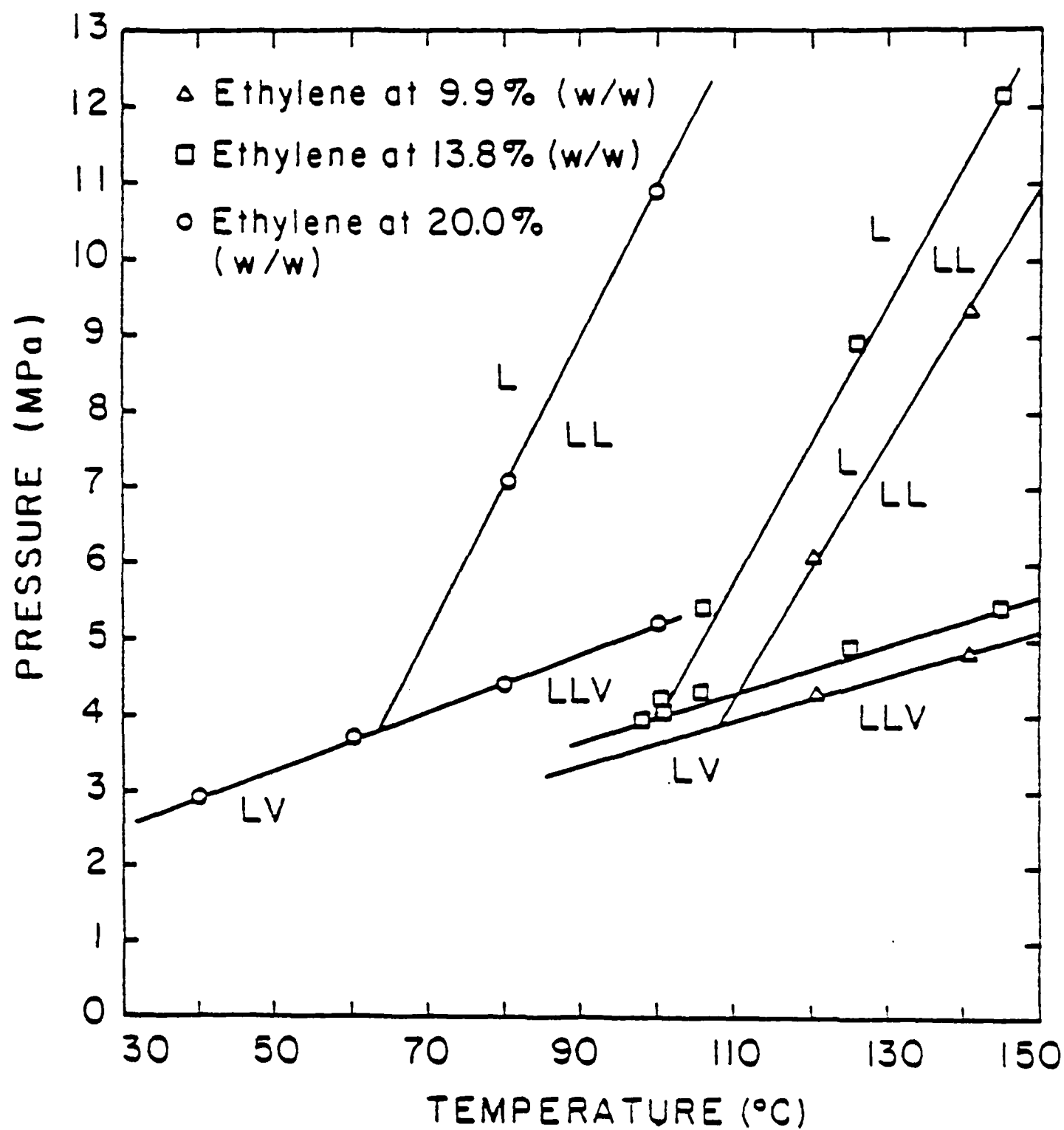23. EP - hexane with no SCF additive
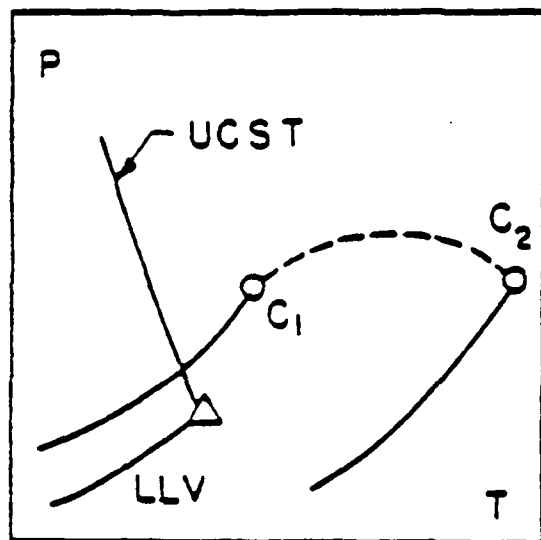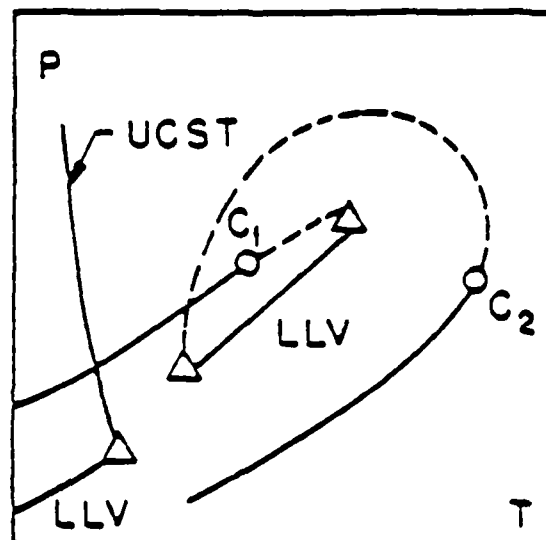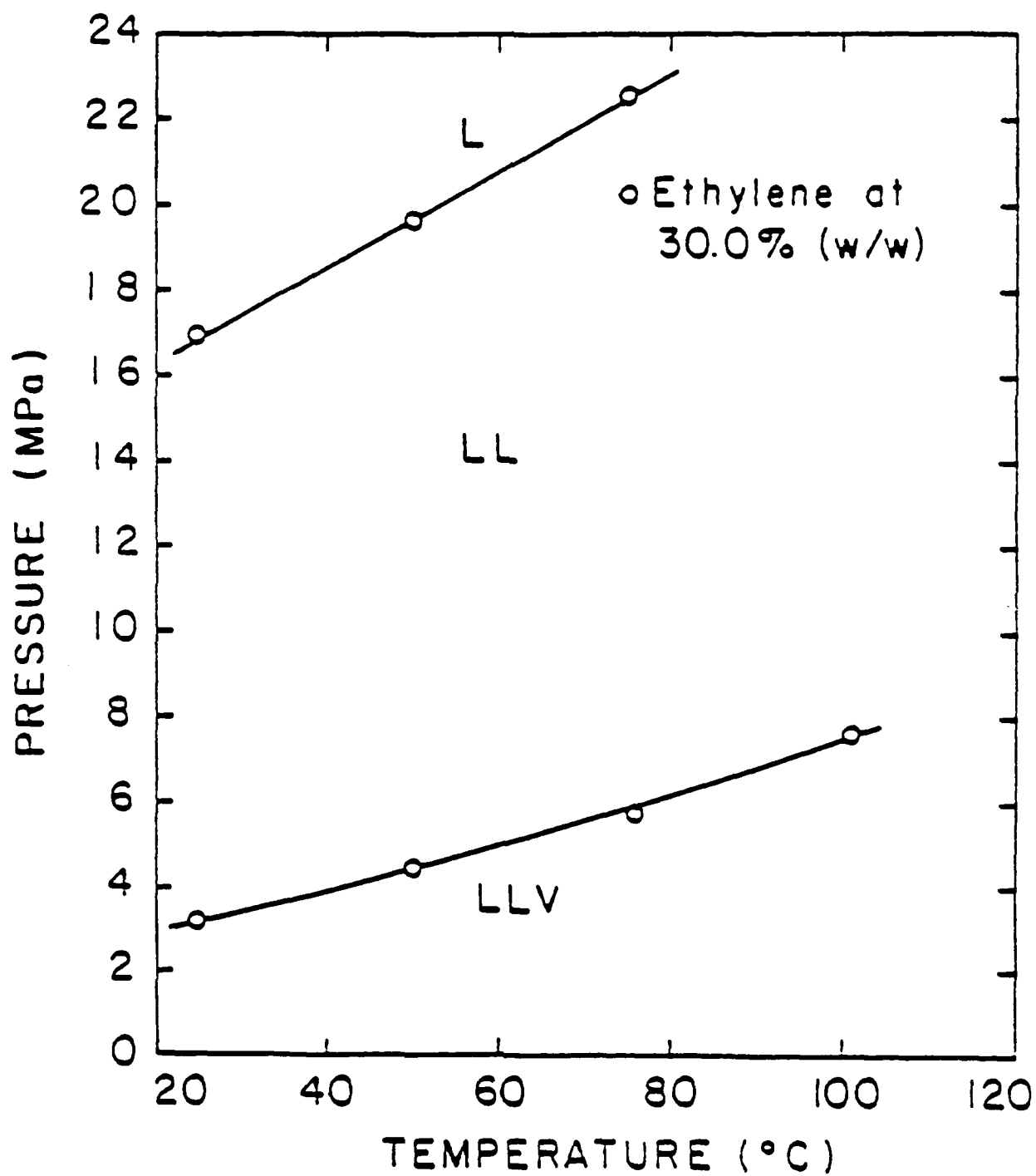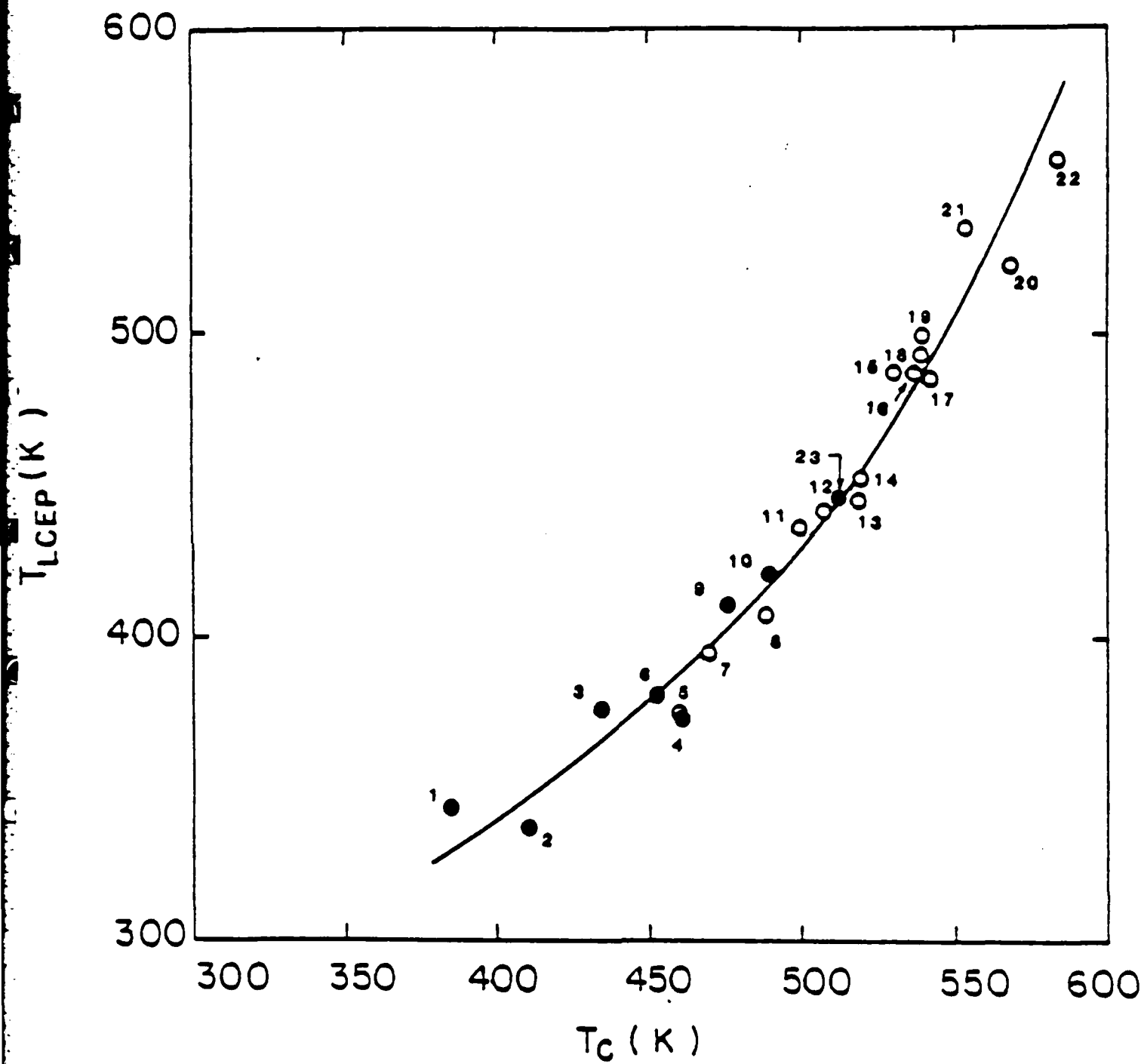
Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Figure 5

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